AD-A153 079 THE SPECTROSCOPY AND REACTION KINETICS OF COORDINATED UNSATURATED METAL CARBONYLS(U) NORTHWESTERN UNIV EVANSTON IL DEPT OF CHEMISTRY E WEITZ 01 NOV 84 1/1

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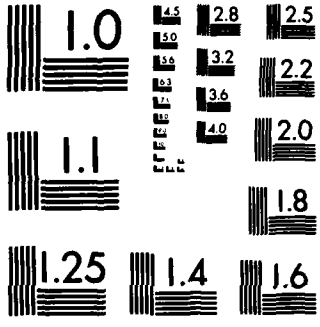

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A program involving the investigation and characterization of reactions of coordinatively unsaturated organometallic species is described. The program emphasizes the measurement of rates of reaction of photolytically produced coordinatively unsaturated species with the parent and rates for cluster formation. Experimental measurements are performed using a time resolved transient absorption apparatus which uses a line tunable CO laser to record spectral and kinetic information by means of probing absorptions in the CO stretch region of the infrared. Systems that have been investigated include coordinatively unsaturated species generated from the $Fe(CO)_5$, $Cr(CO)_6$ and $Mn_2(CO)_{10}$ parents. The results of experiments with these systems are briefly discussed.

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The Spectroscopy and Reaction Kinetics of Coordinated Unsaturated Metal Carbonyls

Eric Weitz
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Coordinatively unsaturated metals are important chemical species with a variety of interesting and unique chemical properties. These species have been shown to be exceedingly reactive. They are important catalysts, reaction intermediates and can form oligomers and metal clusters containing multiple metal centers. Despite their importance and the interest in this area, little is known regarding details of the structure or reactivity of coordinatively unsaturated metals. Their extreme reactivity has heretofore been an impediment to detailed study of these species in the liquid phase and has virtually precluded study in the gas phase. Until recently nothing was known about the mechanism or kinetics for reactions or cluster formation in these systems.

In an effort to alter that situation we have developed an apparatus and a technique which allows us to study coordinatively unsaturated metals in either phase in real time. The use of transient absorption spectroscopy has allowed us to detect and monitor coordinatively unsaturated metals. Briefly, the coordinatively unsaturated metals are generated via excimer laser photolysis of appropriate precursors. Most of our work to date has involved volatile metal carbonyls which are photolyzed to yield gas phase coordinatively unsaturated metal carbonyls or metal atoms. In its present form, the apparatus employs a line tunable CO laser, as a probe, to monitor the change in

absorption of the sample following the excimer laser photolysis pulse. This process is repeated for different laser frequencies with the time versus absorbance signal digitized via a transient digitizer which feeds the data to a signal averager from which it is fed to a computer. The computer takes all the frequency dependent data and assembles it into a transient absorption spectrum which can be displayed as a function of time following the photolysis pulse. Once features in the transient absorption spectrum are identified, a specific feature can be monitored as a function of time and its kinetic behavior discerned. Our current apparatus has a time response of 30 nsec and a typical detection sensitivity corresponding to 10^9 coordinatively unsaturated metal carbonyl molecules.

With the above technique, we have been able to obtain the first gas phase infrared spectrum of a coordinatively unsaturated metal.[1] We have obtained infrared spectra in the CO stretch region for the species $Fe(CO)_x$ (x = 2,3,4) and have measured the rate of reaction of $Fe(CO)_x$ with CO and the activation energies for these reactions.[2] We have made the first real time observation of and are measuring the kinetics for clustering of $Fe(CO)_x$ species.[3] We are also investigating the inhibition of clustering on addition of other ligands to the system. We have performed similar studies for the $Cr(CO)_6$ system, looking at spectra for $Cr(CO)_x$ (x = 2,3,4,5) and have measured rates of reactions of $Cr(CO)_5$ with CO, CH_4, N_2, H_2 and C_6H_6.[4] We have also observed a heretofore unreported clustering process in the $Cr(CO)_x$ system and are investigating details of the mechanism for this process. We have begun work on the $Mn_2(CO)_{10}$ system with the objective of measuring product distributions following photolysis at 193, 249 and 351 cm^{-1}.[5] The rate of reaction of

ligands with the photofragments will be measured as will the rate for reformation of $Mn_2(CO)_{10}$ from two $Mn(CO)_5$ fragments. This latter measurement will be the first measurement for the rate of formation of a metal-metal bond in the gas phase.

1. A. J. Ouderkirk, P. Wermer, N. L. Schultz and E. Weitz, J. Am. Chem. Soc. 105, 3354 (1983).

2. A. J. Ouderkirk and E. Weitz, J. Chem. Phys. 79, 1089 (1983).

3. A. J. Ouderkirk, T. Seder and E. Weitz, work in progress.

4. T. A. Seder, S. P. Church, A. J. Ouderkirk and E. Weitz, submitted for publication.

5. T. A. Seder, S. P. Church and E. Weitz, work in progress.

Publications Supported Under This Contract

a) Gas Phase Photofragmentation of $Cr(CO)_6$: Time Resolved Infrared Spectrum and Decay Kinetics of "Naked" $Cr(CO)_5$.
T. A. Seder, Stephen P. Church, A. J. Ouderkirk and Eric Weitz.
Submitted to J.A.C.S.

b) The Spectroscopy and Reaction Kinetics of Photolytically Generated Coordinatively Unsaturated Organometallics in the Gas Phase: $Fe(CO)_x$ (x = 2,3,4).
T. A. Seder, A. J. Ouderkirk and Eric Weitz.
Manuscript in preparation, planned journal J.A.C.S.

c) Gas Phase Photofragmentation of $Mn_2(CO)_{10}$: Nascent Product Distribution, Spectroscopy and Recombination Kinetics.
T. A. Seder, Stephen P. Church and Eric Weitz.
Manuscript in preparation, planned journal J.A.C.S.

d) The Generation and Detection of Coordinatively Unsaturated Organometallic Species.
Martyn Poliakoff and Eric Weitz.
To be published in Annual Review of Organometallic Chemistry.

Associated personnel

T. A. Seder - graduate student
S. P. Church - postdoctoral research associate
J. T. Knudtson - visiting scholar

Papers presented relating to project area

Seminars:	Dow Chemical Co.	10/83
	University of Nottingham (England)	2/84
	University of Colorado	4/84
	Northwestern University Industrial Affiliates Program	4/84
	CRDC Laboratory - Aberdeen Provings Ground	7/84
Meetings:	SPIE Symposium on Industrial Application of Lasers - Los Angeles	1/84
Workshops:	AFOSR Workshop on Spacecraft Survivability Aberdeen Provings Ground	7/84

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